

HETEROPOLYANIONS, SOLUBLE PRECATALYSTS FOR QUINOLINE HYDROGENATION.

Sang-Man Koo, M.L. Hoppe, and R. M. Laine
The Department of Materials Science and Engineering and
the Department of Chemistry, University of Michigan,
Ann Arbor, MI. 48109-2136

Keywords: Heteropolyanions ; Quinoline Hydrogenation ; Bimetallic Catalyst Precursors.

Within the past two decades, inorganic chemists have developed a growing fascination for metal cluster chemistry, especially metal cluster catalysis chemistry. The sources of this fascination are the potential benefits cluster catalysis can provide to: (1) further the development and understanding of heterogeneous catalysis through modeling studies; (2) advance the development of new, industrially important, homogeneous catalysis chemistry, and (3) provide a sound basis for the development of "surface confined" metal cluster catalysis chemistry. The latter area being the translation of metal cluster catalysis chemistry to the development of new heterogeneous catalysts.

In this study, we describe initial efforts to evaluate a set of heteropolyanions (HPAs, $[EM_{12}O_{40}]^{4-}$ where E = P and M = Mo or W, Mo-HPA, W-HPA) as potential liquefaction and hydrotreating catalysts. We develop a standard set of reaction parameters for quinoline (Q) hydrogenation to tetrahydroquinoline (THQ) by delineating the effects of variations in temperature, H_2 pressure, catalyst and Q concentrations on the catalytic activity of a set of precatalysts. These standard parameters are then used to survey other potentially useful catalysts.

At the outset, it was anticipated that soluble HPAs would serve as precatalysts to the true, active species. It was also recognized that under the reaction conditions employed, the soluble HPAs might be transformed to heterogeneous species. We find that under the reaction conditions employed; the precatalysts described here, decompose to give heterogeneous catalyst particles that actively catalyze hydrogenation of Q to THQ. The following studies establish the parameters of the process leading to formation of active catalyst and define conditions used to survey of other potential catalysts.

The effects of variations in H_2 pressure (P_{H_2}) on catalyst activity are shown in Figure 1. There appears to be an almost linear relationship between H_2 pressure and catalyst activity (turnover frequency, TF).¹ Under the conditions studied, it was not possible to ascertain the P_{H_2} required to reach the falloff region, where the relationship TF/P_{H_2} is no longer linear.

Figure 2 shows the effect of total metal concentration on catalyst activity for Mo-HPA.

The highest catalyst concentration used in this study (5.5×10^{-4} M) is less than 0.02 mole percent of the Q concentration used. Within the range of catalyst concentrations studied, except at very low concentrations, there appears to be a linear relationship between catalyst concentration and TF. These results are extremely valuable because, as discussed below, the active catalyst is heterogeneous. At low metal concentrations, the linearity of the conc./TF relationship is lost because of errors in reproducibility at very low conversions.

The Figure 3 results indicate that under the reaction conditions studied, the rate of Q hydrogenation to THQ is not linearly dependent on initial Q concentration. The turnover frequency reaches its maximum (TF = 20) at $[Q] = 4.23$ M at $[Mo-HPA] = 5.5 \times 10^{-4}$ M. Considering the extremely high Q concentrations used, there are three likely explanations for the observed falloff. One is that above $[Q] = 4.23$ M, the reaction conditions are pseudo first order, with H_2 pressure being the only variable and the falloff above these concentrations resulting from experimental error. Alternately, at these high concentrations, Q competes successfully with H_2 for active catalyst sites thereby slowing the rate of hydrogenation. A third explanation is that at these high Q concentrations, the reaction solution composition is quite different--there is much less EtOH. Consequently, the solvation of the precatalyst changes or the decomposition mechanism and therefore the surface area of the active catalyst produced is diminished.

Initial rates of reaction were determined for each temperature from 150 to 225°C with initial H_2 pressures of 400 psig. Raw reaction rate data are used to calculate initial TFs which are used as k_{obs} .¹ These data allow us to calculate an activation energy of $E_a = 16 \pm 3$ kcal/mole.

Figure 4 indicates that the bimetallic Mo-HPA/ $RuCl_3 \cdot xH_2O$ precatalyst system offers the highest catalytic activity (TF ~ 10) of the precatalysts surveyed. The absence of catalytic activity for W-HPA and $(NH_4)VO_3$ were somewhat unexpected considering the modest activities of the polyoxomolybdate catalysts.

The baseline studies presented above were conducted to: (1) develop a set of standard conditions for testing HPA precatalyst systems; (2) identify promising precatalysts for further study at higher temperatures, and (3) establish hydrogenation reactivity patterns of the prospective catalyst systems. These studies were designed to answer several important questions concerning the utility of HPAs as hydrotreating and hydroliquefaction precatalysts. The questions include: (1) Do HPA derived catalysts function as heterogeneous or homogeneous catalysts?; (2) What advantages do HPAs offer over conventional catalysts?; and (3) Are polymetallic HPA derived catalysts better than conventional or monometallic HPA catalysts?

How Do HPA Derived Catalysts Function: As noted above, the HPA systems function as heterogeneous catalysts rather than homogeneous catalysts. Proof of heterogeneity comes from the fact that catalyst activation requires: (1) hydrogen reduction; (2) CS₂, and (3) an induction period (10-15 min at 200°C) prior to onset of catalyst activity. All of these components are necessary to obtain catalytic activity. In addition, once the heterogeneous catalyst has been formed, removal of all of the reaction solution (by decantation in air) followed by readdition of more Q and EtOH (but not CS₂) and repressurization to the initial H₂ pressure, gives the same catalyst activity as obtained initially--without an induction period. Thus, the heterogeneous particles formed by reduction, sulfidation and degradation of the HPAs is the true, active catalyst. One important observation is that there is a linear correlation between precatalyst concentration and catalyst activity (Figure 2). This linear relationship occurs despite the fact that catalysis occurs after conversion of the homogeneous precatalyst to the active, heterogeneous form.

It can be argued that increases in precatalyst concentration should lead to lower, relative catalyst surface areas (leading to lower TF/mole metal) as initially nucleated catalyst particles serve as growth sites for the decomposition of additional HPA molecules. Given that the correlation is linear, we presume that nucleation is a solution phase rather than a surface phenomena. Thus, all of the catalyst particles may be expected to be of approximately the same dimensions. Scanning electron microscopy supports this idea, given that the fresh catalyst particles, seen at highest magnification, are all submicron and therefore offer very high surface areas.

What Advantages Do HPAs Offer Over Conventional Catalysts: Several potential advantages are offered by HPAs relative to conventional catalysts. First, HPAs are soluble in a variety of polar and slightly polar solvents including water, MeOH, EtOH, and acetonitrile. Consequently, under liquefaction conditions, it should be possible to tailor the HPA/solvent system to optimize coal swelling and coincidentally catalyst dispersion. By comparison, conventional soluble catalysts such as ammonium heptamolybdate; which exhibits essentially the same activity as Mo-HPA (see Figure 4), is soluble only in water.

Bimetallic HPAs were also examined. Surprisingly, studies with the bimetallic precatalyst,² (NH₄)₆[Co₂Mo₁₀O₃₈H₄]·7H₂O, reveal catalytic activities somewhat less than exhibited by Mo-HPA and the heptamolybdate on a per-mol of metal basis. The most likely explanation is that the effectiveness of "CoMo" and NiMo bimetallic catalysts derives from their ability to promote C-N bond hydrogenolysis rather than hydrogenation of Q to THQ. Indeed, one could argue from our data on Mo-HPA, (NH₄)₆[Co₂Mo₁₀O₃₈H₄]·7H₂O, and the heptamolybdate that hydrogenation of Q must occur almost entirely on sulfided molybdenum sites. The bimetallic compound, (NH₄)₆[Co₂Mo₁₀O₃₈H₄]·7H₂O,² with some cobalt should

generate catalyst particles with some portion of the surface "protected" by cobalt. Consequently, if sulfided molybdenum sites are indeed responsible for hydrogenation and surface areas are comparable, one would expect the $(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4] \cdot 7\text{H}_2\text{O}$ derived catalyst to exhibit lower TFs for Q hydrogenation, as observed.

Polymetallic HPA Precatalysts vs Conventional or Monometallic HPA Precatalysts: We have conducted one set of tests based on our previous discovery that RuMo bimetallic systems were exceptionally active HDN systems.³ Our previous studies were conducted with the objective of optimizing Ru/CoMo/ α -alumina catalysts for the HDN of Q to propylbenzene.³ It was assumed that the major function of Ru in this trimetallic system is to promote C-N bond cleavage at low temperatures. Limited efforts were made to determine the effects of ruthenium on the individual metals (Co and Mo) with the finding that a RuMo organometallic surface confined catalyst exhibits the same synergistic activity for production of propylbenzene as the trimetallic catalyst. However, no effort was made to explore the effects of Ru on Q hydrogenation activity in this catalyst system.

Figures 5 and 6 show Q to THQ conversions as a function of time for typical reactions run using Ru/Mo-HPAs bimetallic systems where Ru is introduced either as RuCl_3 or $\text{Ru}_3(\text{CO})_{12}$, and for the individual precatalysts. These Figures also show the simple sums of the conversion percentages of the individual catalysts for comparison with the true bimetallic catalysts. In both instances, the actual bimetallic catalyst offers activities some 20% higher than the sums of the two metals used individually. The results clearly point to a synergistic system. However, it is too early to speculate on the reasons for these results.

Hydrogenation Modeling Studies vs HDN Activity vs. Coal Liquefaction Behavior. The RuMo precatalyst system, which shows good Q to THQ conversion activity, was studied based on the exceptional abilities of a supported RuMo material to promote THQ HDN catalysis as previously reported from these laboratories.³⁻⁸ Although it is tempting to claim that the hydrogenation activities parallel the previously observed C-N bond hydrogenolysis activities, we believe that the parallel is coincidental. For example, both Rh and Pd catalysts are quite effective hydrogenation catalysts but exhibit only moderate HDN activity.^{9,10}

The current studies with a Ru/Mo-HPA precatalyst system works well and will be explored extensively in the future. However, this system can only serve as a baseline for liquefaction studies because the precatalyst system consists of a mixture of soluble forms of both Ru and Mo. In direct liquefaction studies, a major concern will be our ability to create the same bimetallic catalyst properties in single particles following impregnation of coal with the two independent, soluble species. We view this as unlikely with the current set of precatalysts.

Acknowledgements

We wish to thank the Department of Energy and the Pittsburgh Energy and Technology Center for generous support of this work through contract no. DE-FG22-90PC90313. We would also like to thank Dr. A. Hirschon of SRI International for helpful discussions.

References

1. k_{obs} at each temperature is obtained from the slope of the equation, $d[\text{THQ}]/dt = k_{\text{obs}}[\text{Q}]^0$, assuming zero order reaction from data obtained. The activation energy, E_a , is calculated from the expression $k_{\text{obs}} = Ae^{(-E_a/RT)}$.
2. G. Tsigdinos, Dissertation Abstract, University of Michigan, B22, 732 (1961)
3. "Modeling the Hydrodenitrogenation Reaction Using Homogeneous Catalyst Model Systems." A. S. Hirschon, R. B. Wilson, Jr.; and R. M. Laine, *New J. Chem.*, **11**, 543-547 (1987).
4. "New Catalysts for Hydrotreating Coal Liquids." A. S. Hirschon, R. B. Wilson Jr., and R. M. Laine, *Am. Chem. Soc. Div. Fuel. Prepr.* **31**, 310-317 (1986).
5. "New Approaches to Enhance Hydrodenitrogenation of Coal Liquids" A. S. Hirschon, R. B. Wilson, Jr., R. M. Laine, in Adv. in Coal Chemistry, Theophrastus Publ, Athens 1988, p 351.
6. "Ruthenium Promoted Hydrodenitrogenation Catalysts." A. S. Hirschon, R. B. Wilson Jr., and R. M. Laine, *J. Appl. Cat.* **34**, 311-316 (1987).
7. "Bulk Ruthenium as an HDN Catalyst", A. S. Hirschon and R. M. Laine, *J. Energy and Fuels* **2**, 292-295 (1988).
8. "Use of Promoters to Enhance Hydrodenitrogenation and Hydrodeoxygenation Catalysis", A. S. Hirschon, L. L. Ackerman, R. M. Laine, and R. B. Wilson, Jr. *Proc. of the 1989 Internat. Conf. on Coal Science, Tokyo.*, Vol. **II**, p. 923.
9. S-I Murahashi, Y. Imada, and Y. Hirai, "Rhodium Catalyst Hydrogenation of Quinolines and Isoquinolines under Water-Gas Shift Conditions", *Bull. Chem. Soc. Jpn.* **62**, 2968 (1989).
10. M. J. Guttieri and W. F. Maier, *J. Org. Chem.* **49**, 2875 (1984).

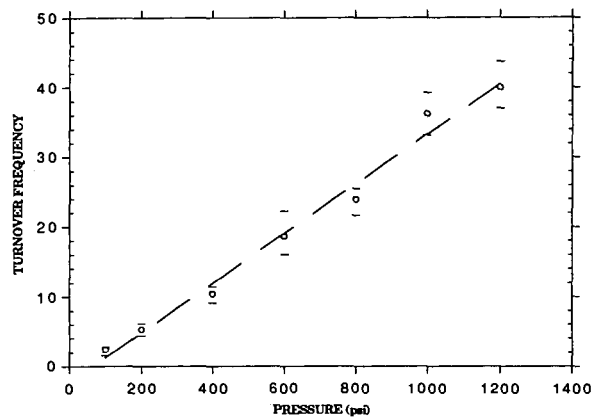


Figure 1. Turnover Frequency as a Function of Initial H₂ Pressure.
Pressures shown are measured at room temperature.

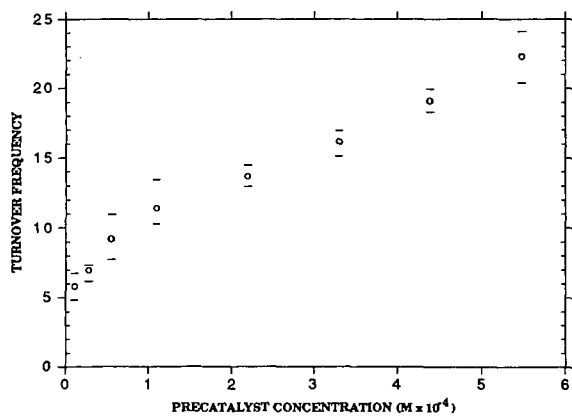


Figure 2. Turnover Frequency as a Function of [Mo-HPA]
Activities were determined based on less than
25 % conversion of Q to THQ

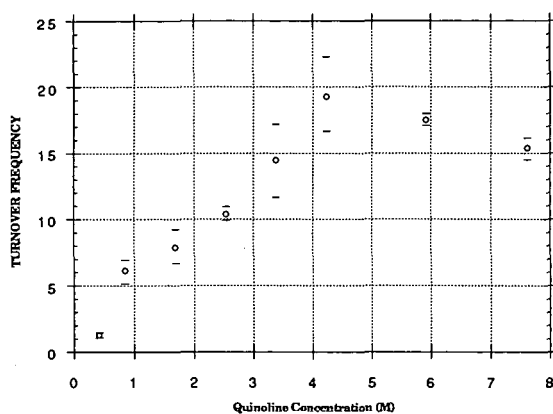


Figure 3. Turnover Frequency as a Function of Changes in [Quinoline]

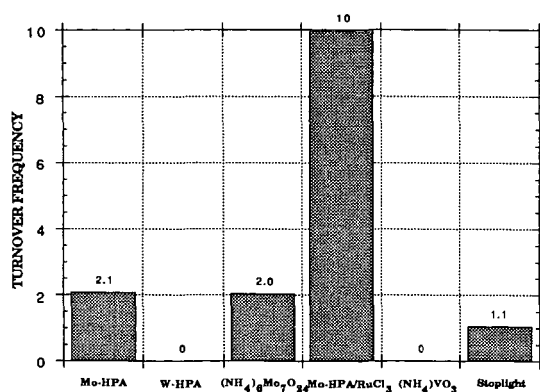


Figure 4. Initial Turnover Frequencies at 175 °C, 400 psig H₂ for Selected Precatalysts. TFs calculated based on total moles of metal. Error limits are + 6%.

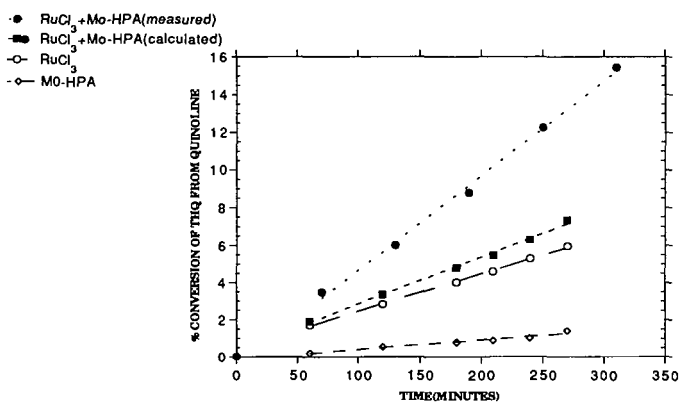


Figure 5. Percent Conversion of THQ from Quinoline for Bimetallic Precatalyst Systems (Mo-HPA , $\text{Mo-HPA}/\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$). Reactions run at 175°C , 400 psiH_2 .

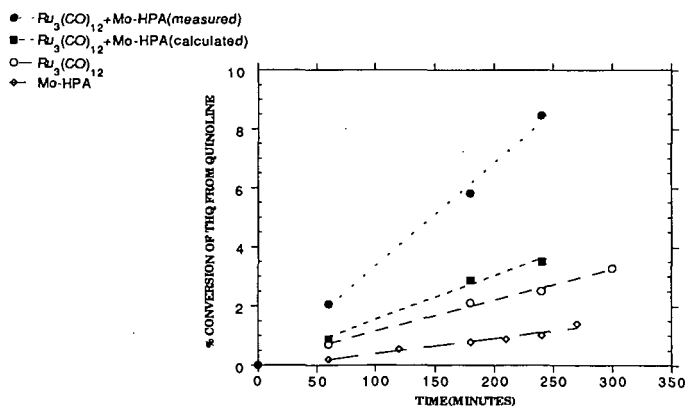


Figure 6. Percent Conversion of THQ from Quinoline for Bimetallic Precatalyst Systems (Mo-HPA , $\text{Mo-HPA}/\text{Ru}_3(\text{CO})_{12}$, and $\text{Ru}_3(\text{CO})_{12}$). Reactions run at 175°C , 400 psiH_2 .